U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-254 580-T

PRESENT-DAY STATE OF INDUSTRIAL HYGIENE PROBLEMS IN HYDROMETALLURGICAL PRODUCTION OF TUNGSTEN AND MOLYBDENUM SALTS AND OXIDES

ENVIRONMENTAL PROTECTION AGENCY

1971

~~161026~~
235026

PB 254 580

BTR-76-198

PRESENT-DAY STATE OF INDUSTRIAL HYGIENE PROBLEMS IN HYDROMETALLURGICAL PRODUCTION OF TUNGSTEN AND MOLYBDENUM SALTS AND OXIDES

[sovremennoye sostoyaniye voprosov gigiyeny truda pri gidrometallurgicheskom sposobe polucheniya soley i okislov vol'frama i molibdena]

By

L. P. Golyakova

Institute of Industrial Hygiene and Occupational Diseases, Leningrad

Published in Gigiyena Truda i Professional'nye Zabolevaniya [Industrial Hygiene and Occupational Diseases] 15 (2) : 4-8, 1971.

This paper discusses issues in the hydrometallurgical production of tungsten and molybdenum salts and oxides of concern to industrial hygiene. The technology used is briefly described and the main adverse factors in the industry under consideration are pointed out with particular emphasis on the pollution of the atmosphere by dust containing W, Mo and SiO_2. High concentrations of irritating gases (NH_3, HCl, H_2S) were recorded in the air in industrial production areas and work sites. Due to existing work conditions, dust induced fibrosis and a high level of chronic afflictions involving the upper respiratory tract were noted among the workers. The paper compares working conditions at two plants with different mechanized technology levels and demonstrates the importance of advanced technology in the improvement of work hygiene in the industry studied.

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

Translated for NERC-Library, EPA, from the Russian, by LEO KANNER ASSOCIATES, P. O. Box 5187, Redwood City, California 94063, (415) 365-3046, October 1975.

BIBLIOGRAPHIC DATA SHEET	1. Report No. TR76-198	2.	3. Recipient's Accession No.
4. Title and Subtitle Present-Day state of industrial hygiene problems in hydrometallurgical production of tungsten and molybdenum salts and oxides			5. Report Date 1971 6.
7. Author(s) Golyakova, L. P.			8. Performing Organization Rept. No.
9. Performing Organization Name and Address Translated from the Russian by the EPA.			10. Project/Task/Work Unit No. 11. Contract/Grant No.
12. Sponsoring Organization Name and Address Translation Section Library Services Environmental Protection Agency Research Triangle Park, N. C. 27701			13. Type of Report & Period Covered 14.

15. Supplementary Notes

Published in Gigiyena Truda i Professional'nye Zabolevaniya 15 (2):4-8,1971.

16. Abstracts

17. Key Words and Document Analysis. 17a. Descriptors

EPAISD

17b. Identifiers/Open-Ended Terms

Soviet Union
Occupational Health
Air Pollution-Health Effects

17c. COSATI Field/Group

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages
This translation was made from a non-copyrighted text.	UNCLASSIFIED	11
	20. Security Class (This Page) UNCLASSIFIED	22. Price 3.50

Modern industry utilizes on an ever-increasing scale refractory metals, including tungsten (W) and molybdenum (Mo). Hydrometallurgical conversion of ore concentrates to tungsten and molybdenum salts and oxides -- the main raw material used to obtain pure metals -- represents one of main production stages (A. N. Zelikman, A. N. Zelikman et al, L. Norcott, Jones, Johnson, et al). The demand for refractory product metals is increasing. Old hydrometallurgical treatment plants are continually modernized and expanded, new plants are under construction, and the number of workers employed by them increases.

The purpose of this study is to investigate the working conditions and the state of health of workers employed in specialized hydrometallurgical plants producing W and Mo salts and oxides.

The concentrates delivered for treatment to the hydrometallurgical plants may contain both metals -- up to 40-60% WO_3 and up to 7-8% MoO_3 (bimetallic concentrate), or 40-60% compounds of one of the two metals mentioned (single-metal concentrate). In addition, the concentrates contain admixtures in various proportions: Silicon compounds (up to 3%), fluorite (up to 17%) and some other elements. The production process in different plants may differ somewhat, both in the technological solution of individual operations and the design of the equipment, depending on the composition of the concentrate, primarily the percentage content of W and Mo and the character of the admixtures.

The studies were made in two plants typical of this type of production: The hydrometallurgical plant in Nal'chike (Plant 1)(treatment of bimetallic concentrates) and the "Pobedit" plant in Ordzhonikidze(Plant 2), (treatment of simple-metal concentrates). The plants studied differed not only

by the production process, but also by the organization of the production process. Plant 1 is a new modern enterprise based on the latest achievements of hydrometallurgy, utilizing on a wide-scale mechanization and automation in the production process, whereas Plant 2, in operation for many years, increased its output every year without substantial modernization of the production process and equipment and expansion of the production areas.

Essentially the production process in the hydrometallurgical treatment of concentrates reduces to the following: Stage 1. Transition of insoluble W and Mo compounds to the soluble state, yielding sodium or ammonia compounds of these metals. Stage 2. Precipitation of various admixtures from sodium tungstate and molybdate solutions, yielding pure metal salts or oxides.

The reaction takes place in the presence of a large number of reagents (ammoniacal liquor, hydrochloric acid, ammomium chloride, sodium sulfide, etc.). Stage 3. Heat and mechanical treatment of finished products -- calcination, drying, mixing, sifting and packing.

2800 analyses of the air and measurements were made during the studies, permitting an evaluation of the present-day state of industrial hygiene in the plants studied. To clarify the interrelation between the working conditions and their effect on the workers, 200 workers who completed their apprenticeship and represented the main skills, were examined medically.

Dust Concentration in Air in Main Work Sites (mg/m^3)

Samples taken at work sites	Plant 1	Plant 2	
	Tungsten-Molybdenum Concentrate	Molybdenum Concentrate	Tungsten Concentrate
During unloading of concentrates and loading in receiving bin	34.0 - 274.0 60.0 - 224.0	1.4 - 15.3 ---	30.0 - 327.0 52.0 - 252.0
In areas where mixture is handed over for further treatment.	Not detected ---	70.0 - 426.0 ---	334.0 - 932.0 ---
During servicing of calcinating and hardening furnaces (charging and discharging of furnaces	0.6 - 22.0 1.5 - 6.1	45.0 -1151.0 127.0 - 880.0	12.4 - 703.0 64.0 - 300.0
Filling and emptying of tanks of different capacities, sifting	9.0 - 104.0 36.0 - 70.0	590.0 - 880.0 224.0 - 464.0	1305.0-2541.0 ---

Remark : Corresponding to each operation, the first row of numbers denotes the maximum ranges in which the dust concentrationsfluctuate and the second row denotes the concentrations encountered most frequently.

Among the set of adverse factors detected during the study, the most important factor is the release of dust and gases into the air. The emission of dust takes place mainly in the first (treatment of concentrates) and last (treatment of W and Mo salts and oxides) stages of the production process.

The dust content present in the air during certain operations in the treatment of concentrates is presented in the table. It is evident from the table that the dust concentrations in both plants vary within a very wide range, and in most cases, they are on the order of several tens and hundreds of milligrams per cubic meter.

Manual or not fully mechanized operations are the main sources emitting the dust in both plants (filling and emptying of various types of mixers and blenders, sifting, packaging, charging and discharging of furnaces, and also operations involving the displacement of powder-forming materials).

Mention should be made of the fact that in Plant 1, due to the higher degree of mechanization of the production process, the number of sources emitting dust is considerably smaller and the dust concentrations are lower.

The dust determined in different stages, differs by its chemical composition. According to our data, the dust from the concentrates contained 22-41% W, 23-40% Mo and 4-20% SiO_2, and the dust emitted during the treatment of the finished products contained 65-78% W, 26-50% Mo and 1-9% SiO_2. We present the W, Mo and SiO_2 concentrations determined in the working areas during the main production operations (in mg/m^3)

		W	Mo	SiO_2
Plant 1	Stage 1	2.0 - 5.0	---	0.5 - 5.0
	Stage 3	6.0 - 32.0	-0.5 - 200.0	0.2 - 0.7
Plant 2	Stage 1	22.0 - 150.0	0.2 - 3.0	3.0 - 25.0
	Stage 3	48.0 - 117.0	27.3 - 30.0	26.0 - 63.0

An analysis of the results obtained from the determination of tungsten, molybdenum and silicon in the air, shows the same regularities as those observed during the hygiene evaluation of the total dust content. The highest metal and dust concentrations were detected in Plant 2. The highest W and Mo concentrations were detected, as anticipated, in stage 3 of the production process in the finished product areas. High concentrations of fluorite, on the order of 15-18 mg/m^3, were detected during the treatment of concentrates containing fluorite compounds (CaF_2). From the hygiene standpoint,

an equally important factor, significant mainly in stage 2 of the production process (in the chemical sectors), is the pollution of the air by various substances forming gases, predominantly irritating gases -- ammonia, hydrogen sulfide and also hydrochloric acid.

The predominant importance of a particular gas, both in regard to the number of sources from which it is emitted and its concentrations in the air, depends on the production process, which in turn depends on the type of final products. For example, in the production of W and Mo ammonia salts, the leading noxious factor is ammonia, whereas other toxic substances (HCl, H_2S) become dominant in the production of acids and oxides of these metals. From the hygiene standpoint, the process involving the ammonia cycle in the production of metal salts and oxides is of particular interest, since in the future it will be the main method used to obtain metals of industrial grade purity.

Ammonia enters the air in practically all operations involving solutions. The main sources from which it is released are filter presses, Nutsche suction filters, reactors, vaporizing equipment, tanks for the storage of solutions, etc. The air is polluted both directly during the reaction or process on the equipment described, especially during the pouring off or pumping of the ammonia solution or pulp. The most frequent ammonia concentration in the working areas was in the range of several tens and hundreds of milligrams per cubic meter.

The gas concentrations were even higher directly above the working surfaces of the equipment and inspection holes while solutions were being decanted and when the production regulations were infringed.

At the present time, the chemical sectors in hydrometallurgical production plants include, along with modern types of equipment, a substantial share of manually operated old equipment which cannot be easily ventilated (frame filter presses, Nutsche filters, etc.). This equipment is a source of constantly released gases, in particular HCl, whose concentration in the air is as high as 91-124 mg/m^3. In addition reactors are also sources releasing HCl. Its concentration in the vicinity of the reactors was 5.2-26.4 mg/m^3.

Hydrogen sulfide, whose concentrations can be as high as 21-124 mg/m^3, enters the air from the equipment during the precipitation of Mo from the sodium molybdate solution or heavy metals utilizing sodium sulfide. The H_2S released into the air depends on the design characteristics of the equipment. Thus, when continuous reactors were replaced by continuously operating equipment, the gas concentrations in the working areas were reduced to the maximum permissible concentration level, or they were not detected at all. During the servicing of calcinating furnaces, the workers are exposed to sulphurous gas concentrations exceeding the maximum permissible dose 3-20 times. The gas released depends on the design of the furnace. For example a larger volume of gas is released from a boiler furnace than from a five hearth furnace used for the same purpose.

In addition to the factors mentioned, the meteorological factor, characterized by a high air temperature, attaining 37-42°C in the summer becomes important in the main production areas (autoclave, furnace and chemical sector), and also the production noise with an intensity level of 95-105 dB and sound energy maximum in the high frequency range (autoclave sector).

A comparison of the data obtained from hygiene and clinical studies (the latter were made by the staff of the Institute's Clinic under the direction of I. D. Makuleva and A. V. Grinberg) made it possible to substantiate the well known correlation between the state of health of the workers and their working conditions. Dust fibrosis of the lungs, whose etiology was occupational, was diagnosed among some workers employed in "dusty" occupations (most cases occurred in Plant 2).

In spite of the small number of cases detected (8.7% of the people studied) and the comparatively good prognosis for the lung fibrosis, the data confirm the hygiene importance of the dust factor in this industry. The possible contraction of occupational lung diseases under the effect of dust containing W or Mo compounds and SiO_2 admixtures is confirmed in the literature (Z. I. Izrael'son and O. Ya. Mogilevskaya, N. V. Mezentseva, V. Z. Khamitova, et al). A high percentage(52%)of chronic diseases of the upper respiratory tract has been detected among people exposed to the effect of irritating dust or gases.

The data obtained can be used as a rational basis for fundamental approaches to the improvement of the work hygiene conditions in hydrometallurgical tungsten and molybdenum production. One main approach is the complex mechanization of all existing manual operations and the replacement of obsolete types of equipment, thus creating a continuous mechanized production line. The main task is the technical solution of these problems on the development level of modern refractory metal hydrometallurgy.

Recommendations pertaining to the most adverse production sites (from the hygiene standpoint) were made during the study in Plant 1. These included: Mechanization of individual operations, improved ventillation and purification of gases before their release into the atmosphere (replacement

of filter presses by FPAKM (expansion unknown: FPA = Petryanov analytical filter) filtration, mechanized discharge of Nutsche suction filters for tungstic acid, redesigned blender ventillation, etc.).

The data obtained from the study were used by Planning Institutes, in particular, by "Kavkazgiprotsvetmet" (Caucasus State Institute for the Planning of Establishments of Nonferrous Metallurgy) in the modernization of the "Pobedit" plant and in the construction of a new shop for the treatment of molybdenum concentrates, and also by the "Gipronikel" Institute (State Institute for the Planning of Nickel Industry Establishments) in the elaboration of a project task in the construction of a new hydrometallurgical plant.

Bibliography

1. Zelikman, A. N., Metallurgiya vol'frama i molibdena (Tungsten and Molybdenum Metallurgy). Moscow, 1949.

2. Zelikman, A. N., Samsonor, G. V. and Krayn, O. Ye., Metallurgiya redkikh metallov. (Metallurgy of Rare Metals), Moscow, 1954, p. 34.

3. Izrael'son, E. I. and Mogilevskaya , O. Ya., Gig. i san. 4, 1949, p. 19.

4. Kaplun, Z. S. and Mezentseva, N. V. ibid, 6, 1959, p. 16.

5. Lukashev, A. A., Materialy 1-y kazakhskoy respublikanskoy nauchnoy konferentsii po voprosam gigiyeny truda i profzabolevaniy (Proceedings of the First Scientific Conference on Problems in Industrial Hygiene and Occupational Diseases in the Kazakh Republic) Karaganda 1963, p. 174.

6. Mezentseva, N. V., Gig. i san. 4, 1959, p. 25.

7. M ogilevskaya, O. Ya., Gig. i san. 9, 1961, p. 18.

8. Khamitova, V. Z., Bor'ba s silikozom (The Struggle Against Silicosis), Moscow, 1959, Vo. 4. p. 76.